

AD-A190 146

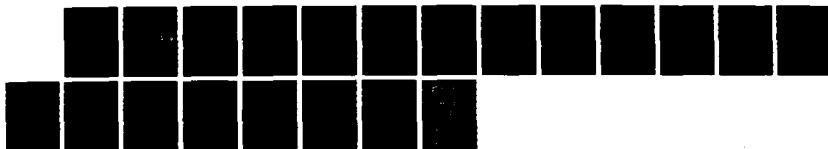
SOLVENT RELAXATION IN THERMAL ELECTRON-TRANSFER  
REACTIONS: SOME COMPARISONS (U) PURDUE UNIV LAFAYETTE IN  
DEPT OF CHEMISTRY G E NICHANIS ET AL. 17 FEB 80 TR-70  
N00014-86-K-0536

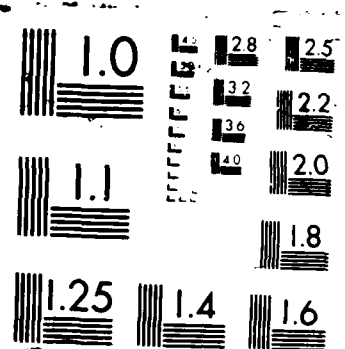
1/1

UNCLASSIFIED

F/G 7/4

ML





AD-A190 146

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0556

Technical Report No. 78

Solvent Relaxation in Thermal Electron-Transfer Reactions:  
Some Comparisons with Real-Time Measurements of  
Solvation Dynamics

by

G. E. McManis and M. J. Weaver

Prepared for Publication

in

Chem. Phys. Lett.

Purdue University

Department of Chemistry

West Lafayette, Indiana 47907

February 17, 1988

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

\* This document has been approved for public release and sale: its distribution is unlimited.

DTIC  
ELECTE  
FEB 29 1988  
S D

## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited.		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 78			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION Purdue University Department of Chemistry		6b OFFICE SYMBOL (If applicable)		7a NAME OF MONITORING ORGANIZATION Division of Sponsored Programs Purdue Research Foundation	
5c ADDRESS (City, State, and ZIP Code) Purdue University Department of Chemistry West Lafayette, IN 47907				7b ADDRESS (City, State, and ZIP Code) Purdue University West Lafayette, IN 47907	
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable)		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO		PROJECT NO	TASK NO
					WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) Solvent Relaxation in Thermal Electron-Transfer Reactions: Some Comparisons with Real-Time Measurements of Solvation Dynamics					
12 PERSONAL AUTHOR(S) G. E. McManis and M. J. Weaver					
13a TYPE OF REPORT Technical		13b TIME COVERED FROM TO		14 DATE OF REPORT (Year, Month, Day) February 17, 1988	
15 PAGE COUNT					
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	solvent relaxation, electron transfer, time-resolved fluorescence ←		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) The role of solvent dielectric relaxation on the barrier-crossing dynamics for outer-sphere electron transfer (ET), as evaluated from the solvent-dependent kinetics of metallocene self-exchange reactions, is compared with recent real-time measurements of polar solvation dynamics obtained from time-dependent fluorescence Stokes shifts (TDFS) for suitable charge-transfer excited states. While the solvent-dependent kinetics obtained in some aprotic media are consistent with the TDFS measurements, the barrier-crossing dynamics in several associated and/or highly polar liquids are indicative of much faster relaxation than inferred from TDFS. The possible nature, and implications, of these rapid modes are discussed.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL			22b TELEPHONE (Include Area Code)		22c OFFICE SYMBOL

(Keywords:)

Solvent Relaxation in Thermal Electron-Transfer Reactions:  
Some Comparisons with Real-Time Measurements of Solvation Dynamics

George E. McManis and Michael J. Weaver

Department of Chemistry

Purdue University

West Lafayette, Indiana 47907, U.S.A.



Attention For	
MS. CRA&I	<input checked="" type="checkbox"/>
MS. EAB	<input type="checkbox"/>
Unpublished	<input type="checkbox"/>
Distribution	
By	
Distribution	
Availability Codes	
Dist	Availability or special
A-1	

Submitted to Chemical Physics Letters.

## ABSTRACT

The role of solvent dielectric relaxation on the barrier-crossing dynamics for outer-sphere electron transfer (ET), as evaluated from the solvent-dependent kinetics of metallocene self-exchange reactions, is compared with recent real-time measurements of polar solvation dynamics obtained from time-dependent fluorescence Stokes shifts (TDFS) for suitable charge-transfer excited states. While the solvent-dependent kinetics obtained in some aprotic media are consistent with the TDFS measurements, the barrier-crossing dynamics in several associated and/or highly polar liquids are indicative of much faster relaxation than inferred from TDFS. The possible nature, and implications, of these rapid modes are discussed.

Although the important role of the solvent medium in determining the free-energy barrier,  $\Delta G^*$ , for electron-transfer processes has long been recognized,<sup>1</sup> its influence upon the barrier-crossing dynamics has only recently been treated theoretically,<sup>2</sup> and subsequently afforded detailed experimental scrutiny.<sup>3,4</sup> By utilizing probe reactions having suitable characteristics (such as a small barrier contribution from intramolecular distortions), and by taking proper account of the variation in  $\Delta G^*$  with the solvent, kinetic data for electron-exchange reactions can yield at least approximate information on the dependence of the barrier-crossing frequency,  $\nu_n$ , upon the solvent properties.<sup>4</sup> Comparison with the corresponding solvent-dependent frequencies predicted from conventional dielectric continuum treatments yields reasonable agreement in some cases,<sup>3</sup> although some substantial deviations between the experimental and predicted frequencies have come to light.<sup>3d,4b,c</sup>

Concurrent with (yet independent of) these activities, real-time measurements of the dynamics of dipolar solvation have been undertaken by utilizing time-dependent fluorescence Stokes shifts (TDFS) for chromophores forming suitable charge-transfer excited states.<sup>5-8</sup> While the majority of these measurements have been restricted to relatively long timescales ( $> 10$  ps) in some recent studies have examined solvent relaxation times down to ca. 0.2 ps.<sup>6a,c,7</sup> Comparisons between the experimental TDFS relaxation times,  $\tau_s$ , and the longitudinal times,  $\tau_L$ , predicted from the dielectric continuum model indicate that typically  $\tau_s \geq \tau_L$ , although multiexponential decay behavior is commonly observed.<sup>6-8</sup>

Prompted in part by these experimental studies, increasing attention is being focused on the manner and extent to which solvent relaxation

attending charge transfer may differ from the conventional dielectric-continuum picture.<sup>6d,9</sup> In particular, mechanisms accounting for multiexponential relaxation have been identified, including the expectation that  $\tau > \tau_1$  for solvent molecules nearby the solute as a consequence of diminished dipole interactions.<sup>6d,9</sup>

Given the current rapid evolution in both experimental and theoretical aspects of charge solvation dynamics, it is clearly of interest to compare these results and concepts with corresponding information on the dynamics of electron-transfer barrier crossing. In particular, there is a need to identify the components of the overall dielectric response having the most relevance to the barrier-crossing problem. Such a comparison is considered here, utilizing our recent data on the solvent-dependent kinetics for metallocene self-exchange reactions.<sup>4c</sup> While necessarily preliminary, we believe that its significance is heightened by the emerging new perspectives of dynamical solvent effects in chemical reactivity.

### Results and Discussion

Unlike TDFS measurements of dielectric solvent relaxation, which are extracted relatively directly from time-dependent Stokes shifts,<sup>10</sup> the evaluation of such effects in the dynamics of barrier crossing for intermolecular electron transfer requires consideration of the influence of barrier energetics upon the observed rate constant,  $k_{ob}$ . A useful formalism for this purpose is expressed as<sup>11,12</sup>

$$k_{ob} = K_p \kappa_{\infty} \nu_n \exp(-\Delta G^*/RT) \quad (1)$$

where  $K_p$  is the equilibrium constant for forming the appropriate



internuclear geometry, and  $\kappa_{01}$  is the electronic transmission coefficient.

We have recently employed this relation to extract solvent-dependent barrier-crossing frequencies,  $\nu_n$ , from  $k_{ob}$  values obtained for metallocene self-exchange reactions using the proton nmr line-broadening technique.<sup>4c,13</sup> These reactions, involving cobalticenium-cobaltocene,  $Cp_2Co^{+/0}$  (Cp = cyclopentadienyl), its decamethyl derivative,  $Cp'_2Co^{+/0}$  (Cp' = pentamethyl-cyclopentadienyl), and ferricenium-ferrocene,  $Cp_2Fe^{+/0}$ , have several virtues for this purpose, as detailed earlier.<sup>4</sup> These include the presence of only small inner-shell (i.e. reactant intramolecular) barriers, small or negligible work-term effects upon  $K_p$ , and the stability and nonspecific solvation of the reactants in a variety of nonaqueous media.

The estimation of absolute  $\nu_n$  values for such electron-exchange processes is hampered not only by uncertainties in  $K_p$  but, most critically, in the  $\Delta G^*$  values. However, relative  $\nu_n$  values in different solvents can be evaluated, at least approximately, since  $K_p$  should be roughly constant and there is good evidence\* that the required solvent dependence of  $\Delta G^*$  can be described for self-exchange reactions by the conventional dielectric continuum formula<sup>14</sup>

$$\Delta G_{os}^* = (e^2/4)(a^{-1} - R^{-1})(\epsilon_{op}^{-1} - \epsilon_s^{-1}) \quad (2)$$

where  $e$  is the electronic charge,  $a$  is the reactant radius,  $R$  is the internuclear distance (commonly presumed to equal  $2a$ ), and  $\epsilon_{op}$  and  $\epsilon_s$  are the optical and static dielectric constants, respectively.

---

\*This includes measurements of optical intervalence transition energies,  $E_{op}$ , in mixed-valence compounds, such as analogs of the metallocenes considered here,<sup>15</sup> in which the solvent-dependent  $E_{op}$  values vary approximately in accordance with Eq (2).<sup>15,16</sup>

The central issue here is the role of solvent dielectric relaxation in the barrier-crossing frequency. While the solvent sensitivity of  $\nu_n$  implies that  $\kappa_{e1} \approx 1$  (i.e. reaction adiabaticity is achieved),<sup>17</sup>  $\nu_n$  may be influenced by reactant vibrations. This contribution, however, is likely to be minor for the present metallocene systems since the inner-shell component of  $\Delta G^*$  is relatively small, ca 10%.<sup>4</sup> Under these circumstances, then, we can simply regard  $\nu_n$  to be related to the effective relaxation time,  $\tau_{eff}$ , by

$$\nu_n = \tau_{eff}^{-1} \quad (3)$$

The comparison between such solvent-dependent  $\tau_{eff}$  values for electron-transfer barrier crossing and corresponding TDFS relaxation times,  $\tau_s$ , forms the objective here.

At least for a Debye fluid (i.e. that having a single relaxation time,  $\tau_D$ ), dielectric continuum treatments of the barrier-crossing dynamics in terms of one-dimensional overdamped motion<sup>2a,b</sup> lead to relations of the type<sup>4a,17</sup>

$$\nu_n = K \tau_L^{-1} \quad (4)$$

where the longitudinal relaxation time  $\tau_L$  is related to  $\tau_D$ , obtained from dielectric loss spectra, by  $\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D$ , with  $\epsilon_\infty$  being the "infinite frequency" dielectric constant. Although the proportionality constant  $K$  in Eq (4) depends somewhat on  $\Delta G^*$  as well as on the shape of the barrier top,<sup>2b</sup> this dependence is relatively mild so that usually  $K$  is within ca twofold of unity for weak-overlap electron exchange.<sup>17</sup> Under these circumstances, then, we expect that  $\tau_{eff}$  can be equated approximately with

$\tau_L$ . A related treatment for solvents exhibiting multiple dielectric relaxation yields the conclusion that  $\tau_{eff}$  is influenced disproportionately by the faster relaxation mode(s), so that  $\tau_{eff} < \tau_{L1}$ , where  $\tau_{L1}$  is the often-predominant "slow" relaxation.<sup>2c</sup> On the other hand, at least for Debye solvents we might anticipate that  $\tau_{eff} > \tau_L$  as a result of short-range solvent contributions to  $\tau_{eff}$ , as noted above.<sup>9a</sup>

Given this situation, it is instructive to examine the solvent-dependent electron-transfer results in the light of the continuum predictions as a preface to comparison with corresponding TDFS data. Table I summarizes rate constants for self exchange,  $k_{ex}$ , for  $Cp_2Co^{+/0}$ ,  $Cp_2'Co^{+/0}$ , and  $Cp_2Fe^{+/0}$  in fifteen solvents, expressed as rate ratios with respect to those in the "reference solvent" dimethylsulfoxide,  $k_{ex}/k_{ex}(ref)$ . The data for the cobaltocene and ferrocene couples are extracted from refs. 4c and 18, respectively. Although the choice of reference solvent is somewhat arbitrary, dimethylsulfoxide was selected since it displays Debye-like dielectric loss behavior<sup>19</sup> and TDFS relaxation kinetics.<sup>6a</sup> Listed alongside are the corresponding  $\tau_{eff}$  estimates for these probes in each solvent, again quoted as ratios to respect to the value in DMSO,  $\tau_{eff}/\tau_{eff}(ref)$ . The latter were obtained from the rate ratios by using [cf. Eq. (1)]:

$$[\tau_{eff}/\tau_{eff}(ref)]^{-1} = [k_{ex}/k_{ex}(ref)] \exp([\Delta G_{os}^* - \Delta G_{os}^*(ref)]/RT) \quad (5)$$

where the  $\Delta G_{os}^*$  estimates were obtained from Eq. (2) (see Table I footnotes). This procedure therefore assumes that  $K_p$  (and  $\kappa_{e1}$ ) are solvent independent (vide supra). While the absolute  $k_{ex}$  values in each solvent are markedly different for the three probe reactions (apparently due to

electronic coupling effects on  $K_p \kappa_{ol}^{13}$ ), the rate and relaxation time ratios are largely similar in a given solvent.

Also listed in Table I are the corresponding longitudinal relaxation time ratios,  $\tau_L/\tau_L(\text{ref})$ , obtained from dielectric loss data. Comparison between the corresponding  $\tau_{eff}/\tau_{eff}(\text{ref})$  and  $\tau_L/\tau_L(\text{ref})$  values reveals that while these ratios are in reasonable agreement (within ca. twofold of each other) in a number of solvents, some substantial discrepancies are present. Most notably, the  $\tau_{eff}$  values in methanol and ethanol are at least 50 fold smaller than expected from  $\tau_L$ . This anomaly has been noted previously on the basis of related electrochemical exchange kinetics.<sup>3d,4b</sup> Qualitatively similar discrepancies between the relative  $\tau_{eff}$  and  $\tau_L$  values are also seen in Table I for propylene carbonate and especially N-methylformamide (NMF).

The TDFS solvation dynamics of four of the solvents in Table I, acetonitrile, DMSO, nitrobenzene, and methanol, have been examined by Castner et al. for timescales down to ca. 0.5 ps using the fluorescence probe LDS-750.<sup>6a</sup> The  $\tau_s$  value in acetonitrile is about tenfold smaller than in DMSO [i.e.  $\tau_s/\tau_s(\text{ref}) \sim 0.1$ ], in rough accordance with the corresponding  $\tau_L$  ratio (Table I), even though  $\tau_s$  is ca. 1.5-2 times  $\tau_L$ .<sup>6a</sup> This behavior is in good accordance with the corresponding  $\tau_{eff}/\tau_{eff}(\text{ref})$  ratios in Table I. The solvation dynamics observed in nitrobenzene and methanol,<sup>6a</sup> however, differ significantly from that expected from the corresponding  $\tau_{eff}$  data in Table I. Biexponential relaxation behavior was obtained in nitrobenzene, with the predominant  $\tau_s$  value being 4 fold smaller than  $\tau_L$ . This yields  $\tau_s/\tau_s(\text{ref}) \sim 0.5$  in this solvent, as compared with  $\tau_{eff}/\tau_{eff}(\text{ref}) \approx 2$  for nitrobenzene and the dielectrically similar solvent benzonitrile (Table I). For methanol Castner et al. found that

$\tau_s/\tau_s(\text{ref}) \approx 1$  which stands in marked contrast to the corresponding relaxation times for barrier-crossing,  $\tau_{eff}/\tau_{eff}(\text{ref}) \approx 0.05$  (Table I). Indeed, the  $\tau_{eff}$  values are indicative of dielectric relaxation in methanol that is at least as rapid as in acetonitrile, whereas the  $\tau_s$  value in the latter solvent is around tenfold shorter than in the latter.<sup>6a</sup>

More striking differences between the barrier-crossing and real-time solvent relaxation behavior are exposed by examining some recent TDFS data obtained using Coumarin 153 as the fluorescence probe.<sup>6b</sup> Although the relaxation timescale was restricted to  $> \text{ca. } 30 \text{ ps}$  in these measurements, and multiexponential decay behavior was typically observed, average  $\tau_s$  values were obtained in propylene carbonate (PC) and N-methylpropionamide (NMP) that are markedly (5-10 fold) longer than the corresponding  $\tau_L$  values. These and other data are indicative of a correlation between  $\tau_s/\tau_L$  and the solvent dielectric constant,  $\epsilon_s$ , since  $\epsilon_s \approx 75\text{-}300$  in PC and NMP under the conditions employed.<sup>6b-d</sup> This behavior is qualitatively in accordance with the MSA treatment of Wolynes,<sup>9a</sup> which predicts that the short-range relaxation time,  $\tau_G$ , is longer than  $\tau_L$  to an extent increasing with  $\epsilon_s$ .<sup>6b</sup> A difficulty, however, is that the likely concomitant changes in  $\epsilon_\infty$  and the solvent size can blur this prediction.

For comparison purposes, a plot of  $\log (\tau_{eff}/\tau_L)$  versus  $\log \epsilon_s$ , where  $\tau_{eff}$  and  $\tau_L$  refer to the relaxation times relative to those in DMSO as listed in Table I, is shown in Fig. 1. The data for each solvent is numbered according to the scheme in Table I. In contrast to the  $\log (\tau_s/\tau_L) - \log \epsilon_s$  behavior noted in ref. 6b, the  $\log (\tau_{eff}/\tau_L)$  values in Fig. 1 are seen to decrease continuously (and roughly linearly) for solvents with progressively higher  $\epsilon_s$  values. In particular, the solvents

having the highest dielectric constants, PC and NMF ( $\epsilon_s = 65$  and 182, respectively), yield  $(\tau_{eff}/\tau_L) \ll 1$ . The only marked divergence is that also  $(\tau_{eff}/\tau_L)$  for methanol and ethanol, even though these solvents exhibit small or moderate  $\epsilon_s$  values. [Although choosing "reference solvents" other than DMSO will alter these ratios, the effect is slight provided that simple aprotic media (e.g. acetonitrile) are selected.]

Taken together, then, these comparisons indicate that *qualitatively different* deviations from the dielectric continuum picture are observed for charge-transfer solvent relaxation in the barrier-crossing and TDFS cases. In particular, for solvents that exhibit substantial hydrogen bonding (methanol, ethanol, NMF) or are highly polar (PC),  $\tau_{eff}$  values are obtained that are unexpectedly short on the basis of the available TDFS results as well as from the dielectric continuum predictions. The most likely explanation for these disparities is that the barrier-crossing dynamics are dominated in these cases by especially rapid relaxation modes that are of insufficient importance to the overall dielectric polarization spectrum and/or refer to timescales that are too short to be detected so far by the TDFS measurements. This line of argument is aided considerably by the likelihood, noted above, that  $\tau_{eff}$  will be influenced disproportionately by such high-frequency components<sup>2c</sup> such that  $\tau_{eff} < \tau_L$ .

The clearcut detection of such modes in dielectric loss spectra, however, is largely thwarted by the paucity of data at sufficiently high frequencies, together with interference from lower-frequency, yet predominant, relaxations.<sup>20</sup> Nonetheless, components having dielectric relaxation times, around 1 ps, much shorter than the major  $\tau_D$  value have been identified for alcohols, including methanol and ethanol,<sup>21</sup> and other

hydrogen-bonded solvents.<sup>22</sup> Translational solvent motion may also provide an important relaxation pathway, at least in methanol.<sup>23</sup> Another candidate relaxation mode is associated with the cooperative rotations and/or librations within solvent cages,<sup>24,25</sup> which are believed to be partly responsible for the difference between  $\epsilon_\infty$  and  $\epsilon_{op}$  for polar fluids.<sup>20</sup> Since the importance of this mode apparently depends on the solvent dipole moment,<sup>20</sup> it may provide an explanation for the form of Fig. 1.

Irrespective of the detailed nature of these fast relaxations, it appears that the slower decay components observed in the TDFS experiments, especially in the more polar and self-associated media, may not contribute importantly (or even significantly) to barrier-crossing dynamics in electron transfer, and by inference in other reactions featuring charge transfer. Given the importance of faster components of the dielectric relaxation, it will be of great interest to attempt the examination of these modes directly in TDFS experiments. Although the TDFS time resolution has previously been largely inadequate for this purpose, the current rapid improvements in subpicosecond laser techniques promise to provide a wealth of such information, of central importance in elucidating dynamical solvent effects in chemical reactions.

#### Acknowledgments

We were aided significantly by helpful discussions and preprints from Ed Castner, Mark Maroncelli, Graham Fleming, Paul Barbara, and John Simon. This work is supported by the Office of Naval Research.

## References

1. R. A. Marcus, J. Chem. Phys., 24 (1956) 966, 979.
2. Representative papers include (a) L. D. Zusman, Chem. Phys., 49 (1980), 295; (b) D. F. Calef, P. G. Wolynes, J. Phys. Chem., 87 (1983), 3387; (c) G. van der Zwan, J. T. Hynes, J. Chem. Phys., 76 (1982), 2993; (d) J. T. Hynes, J. Phys. Chem., 90 (1986), 3701; (e) W. Nadler, R. A. Marcus, J. Chem. Phys., 86 (1987), 3906.
3. For example, (a) M. J. Weaver, T. Gennett, Chem. Phys. Lett., 113 (1985), 213; (b) W. Harrer, G. Grampp, W. Jaenicki, Chem. Phys. Lett., 112 (1984), 263; (c) A. Kapturkiewicz, M. Opallo, J. Electroanal. Chem., 185 (1985), 15; (d) M. Oppallo, J. Chem. Soc. Far. Trans. I, 82 (1986), 339; (e) G. Grampp, W. Harrer, W. Jaenicke, J. Chem. Soc. Far. Trans. I, 83 (1987), 161.
4. (a) T. Gennett, D. F. Milner, M. J. Weaver, J. Phys. Chem., 89 (1985), 2787; (b) G. E. McManis, M. N. Golovin, M. J. Weaver, J. Phys. Chem., 90 (1986), 6563; (c) R. N. Nielson, G. E. McManis, M. N. Golovin, M. J. Weaver, J. Phys. Chem., submitted.
5. (a) D. Huppert, H. Kanety, and E. M. Kosower, Disc. Far. Soc., 74 (1982), 161; (b) E. M. Kosower, J. Am. Chem. Soc., 107 (1985), 1114.
6. (a) E. W. Castner, Jr.; M. Maroncelli, G. R. Fleming, J. Chem. Phys., 86 (1987), 1090; (b) M. Maroncelli, G. R. Fleming, J. Chem. Phys., 86 (1987), 6221; (c) M. Maroncelli, E. W. Castner, Jr., S. P. Webb, G. R. Fleming, in "Ultrafast Phenomena V", G. R. Fleming, A. E. Siegman (eds.), Springer-Verlag, Berlin, 1986, p. 303; (d) E. W. Castner, Jr., B. Bagchi, M. Maroncelli, S. P. Webb, A. J. Ruggiero, G. R. Fleming, Ber. Bunsen. Phys. Chem., in press.
7. (a) V. Nagarajan, A. M. Brearley, T.-J. Kang, P. F. Barbara, J. Chem. Phys., 86 (1987), 3183; (b) M. A. Kahlow, T.-J. Kang, P. F. Barbara, J. Chem. Phys., in press; (c) M. A. Kahlow, T.-J. Kang, P. F. Barbara, J. Phys. Chem., in press.
8. S.-G. Su, J. D. Simon, J. Phys. Chem., 91 (1987), 2693.
9. (a) P. G. Wolynes, J. Chem. Phys., 86 (1987), 5133; (b) R. F. Loring,



- S. Mukamel, J. Chem. Phys., 87 (1987), 1272; (c) E. W. Castner, G. R. Fleming, B. Bagchi, Chem. Phys. Lett., submitted.
10. (a) G. van der Zwan, J. T. Hynes, J. Phys. Chem., 89 (1985), 4181; (b) B. Bagchi, D. W. Oxtoby, G. R. Fleming, Chem. Phys., 86 (1984), 257.
  11. For a review, see N. Sutin, Prog. Inorg. Chem., 30 (1983), 441.
  12. J. T. Hupp, M. J. Weaver, J. Electroanal. Chem., 152 (1983), 1.
  13. R. N. Nielson, M. N. Golovin, G. E. McManis, M. J. Weaver, J. Am. Chem. Soc., in press.
  14. R. A. Marcus, J. Chem. Phys., 43 (1965), 679.
  15. M. J. Powers, T. J. Meyer, J. Am. Chem. Soc., 100 (1978), 4393.
  16. For a review, see C. Creutz, Prog. Inorg. Chem., 30 (1983), 1.
  17. G. E. McManis, A. K. Mishra, M. J. Weaver, J. Chem. Phys., 86 (1987), 5550.
  18. E. S. Yang, M.-S. Chan, A. C. Wahl, J. Phys. Chem., 84 (1980), 3094.
  19. (a) H. Behret, F. Schmithals, J. Barthel, Z. Phys. Chem., 96 (1975), 73; (b) V. Elie, Bull. Soc. Chem. Belg., 93 (1984), 839.
  20. N. E. Hill, W. E. Vaughan, A. H. Price, M. Davies, "Dielectric Properties and Molecular Behavior", Van Nostrand Reinhold, London, 1969, Chapters 1, 5.
  21. J. A. Saxton, R. A. Bond, G. T. Coats, R. M. Dickinson, J. Chem. Phys., 37 (1962), 2132.
  22. For reviews, (a) J. Crossley, Adv. Mol. Relax. Processes, 2 (1970), 69; (b) E. Jakusek, L. Sobezyk, in "Dielectric and Molecular Relaxation Processes", Vol. 3, M. Davies, ed., Chemical Society, 1977, Chapter 4.
  23. G. van der Zwan, J. T. Hynes, Chem. Phys. Lett., 101 (1983), 367.
  24. N. E. Hill, Proc. Phys. Soc., 82 (1963), 723.
  25. For example, (a) J. K. Vij, F. Hufnagel, Chem. Phys. Lett., 139 (1987), 77; (b) J. K. Vij, F. Hufnagel, Adv. Chem. Phys., 63 (1985), 775.

TABLE I. Relative Solvent Dielectric Relaxation Times,  $\tau_{\text{eff}}$ , as Inferred from Rates of Metallocene Self-Exchange Reactions at 25°C.

Solvent <sup>a</sup>	$\Delta G_{\text{os}}^{*b}$ kcal mol <sup>-1</sup>	$k_{\text{ex}}/k_{\text{ex}}(\text{ref})^c$		$\tau_{\text{eff}}/\tau_{\text{eff}}(\text{ref})^g$		$\tau_L/\tau_L(\text{ref})^h$
		$\text{Cp}_2\text{Co}^{+/o d}$	$\text{Cp}_2\text{Co}^{+/o e}$	$\text{Cp}_2\text{Co}^{+/o d}$	$\text{Cp}_2\text{Co}^{+/o e}$	
1. DMSO	4.8	(1.9 x 10 <sup>8</sup> )	(2.4 x 10 <sup>7</sup> )	(1.6 x 10 <sup>6</sup> )		
2. Acetonitrile	5.75	2.3	1.6	3.3	0.10	0.06
3. Acetone	5.4	1.2	0.8	2.9	0.3	0.12
4. CH <sub>2</sub> Cl <sub>2</sub>	4.2		3.7	2.7		0.17
5. (CH <sub>2</sub> Cl) <sub>2</sub>	4.15		2.6	2.7		0.65
6. Pyridine	4.0		1.9		2.0	0.5
7. DMF	5.05	1.1	1.1		0.6	0.55
8. NMF	5.3		2.8		0.15	1.5
9. PC	5.25	1.5	1.2		0.3	1.1
10. Benzonitrile	4.2	1.3	2.5		2.1	2.4
11. Nitrobenzene	4.2			1.4		2.2
12. TMU	4.75		0.5		2.2	~ 2.5
13. HMPA	4.75	0.19	0.22		4.5	3.7
14. Methanol	5.85		3.0	3.8	0.06	0.05
15. Ethanol	5.45		2.5		0.13	9.2

Footnotes to Table I

<sup>a</sup> DMSO - dimethylsulfoxide;  $\text{CH}_2\text{Cl}_2$  - dichloromethane;  $(\text{CH}_2\text{Cl})_2$  - 1,2-dichloroethane; DMF - N,N'-dimethylformamide; NMF - N-methylformamide; PC - propylene carbonate; TMU - tetramethylurea; HMPA - hexamethylphosphoramide.

<sup>b</sup> Outer-shell (i.e. solvent) reorganization energy for self-exchange reactions in a given solvent, estimated from Eq. (2), with  $a = 3.8 \text{ \AA}$ ,  $R = 2a$ , and using literature dielectric constant data (see ref. 4 for details).

<sup>c</sup> Ratio of observed rate constants for self exchange of listed redox couple in given solvent to that in dimethylsulfoxide, obtained by proton nmr line broadening technique.<sup>4c,13,18</sup> Ratios for  $\text{Cp}_2'\text{Co}^{+/0}$  from ref. 4c, and for  $\text{Cp}_2\text{Fe}^{+/0}$  from ref. 18. Quantities listed in parentheses are absolute values of  $k_{\text{ex}}$  ( $\text{M}^{-1} \text{ s}^{-1}$ ) measured in DMSO. (For  $\text{Cp}_2'\text{Co}^{+/0}$  and  $\text{Cp}_2\text{Co}^{+/0}$ , each solvent contained 0.1 M tetraethylammonium tetrafluoroborate.<sup>7c,13</sup>)

<sup>d</sup>  $\text{Cp}_2'\text{Co}^{+/0}$  - decamethylcobaltocenium-decamethylcobaltocene.

<sup>e</sup>  $\text{Cp}_2\text{Co}^{+/0}$  - cobaltocenium-cobaltocene.

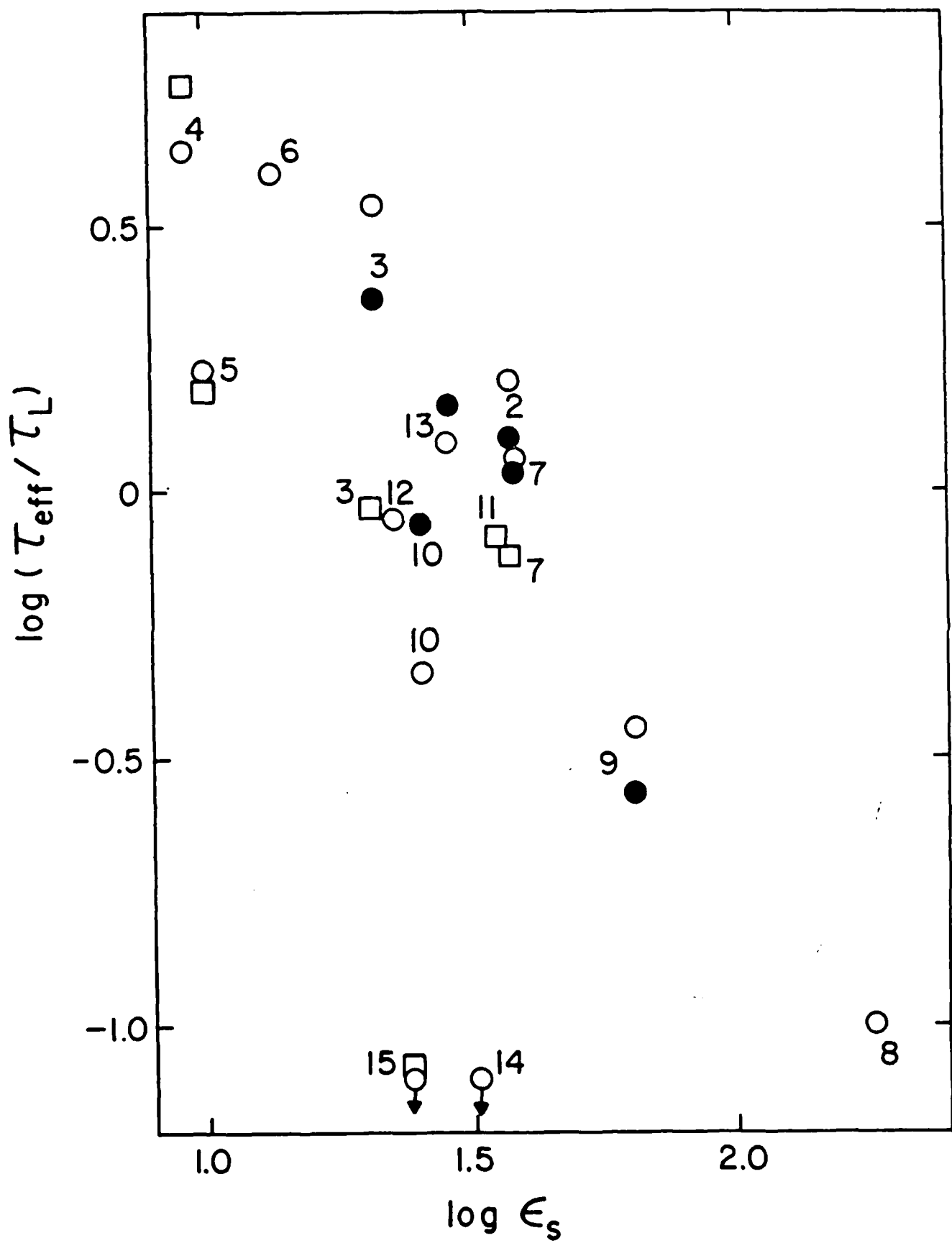
<sup>f</sup>  $\text{Cp}_2\text{Fe}^{+/0}$  - ferrocenium-ferrocene.

<sup>g</sup> Ratio of effective relaxation time for barrier crossing in given solvent to that in the "reference solvent", dimethylsulfoxide. Obtained from corresponding  $k_{\text{ex}}/k_{\text{ex}}(\text{ref})$  values and  $\Delta G_{\text{ex}}^*$  estimates using Eq. (5). (See text for details.)

<sup>h</sup> Ratio of longitudinal relaxation time in given solvent to that in dimethylsulfoxide. Obtained from experimental Debye relaxation times,  $\tau_D$ , by using  $\tau_L = \tau_D (\epsilon_\infty/\epsilon_s)$  (see ref. 4 for details and literature sources).

Caption to Fig. 1

Logarithm of ratio of effective relaxation time for barrier crossing in metallocene self exchange reactions,  $\tau_{eff}$ , to longitudinal relaxation time in a given solvent,  $\tau_L$ , versus the logarithm of the static dielectric constant. Ratios taken with respect to values in dimethylsulfoxide; see text for calculational details. Key to reactions: filled circles,  $Cp_2Co^{+/0}$ ; open circles,  $Cp_2Co^{+/0}$ ; open squares,  $Cp_2Fe^{+/0}$ . See Table I for key to solvent numbers and reactant symbols.



END  
DATE  
FILMED

4-88

DTIC